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Thermodynamics of liquid mixtures of acids. Vapour–liquid equilibria and excess molar enthalpies of alkanoic acid mixtures with alcohols

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Abstract

Vapour–liquid equilibria and excess molar enthalpies of binary solutions of methanoic acid, ethanoic acid, propanoic acid, and butanoic acid with methanol, ethanol, propanols, and 1-butanol were calculated using the UNIQUAC associated-solution model, which takes into account the homo-association of like molecules and the hetero-association of unlike molecules. Ternary excess molar enthalpies of ethanoic acid + methanol + tetrachloromethane were predicted from the same model with binary parameters. The calculated results agree well with the experimental values.

LIST OF SYMBOLS

A, A_1, A_2	acid, acid monomer and dimer
a_{JI}	binary interaction parameter for J–I pair
AB_i	chemical complex involving an acid and alcohol i-mer
B, B_1, B_i	alcohol, alcohol monomer and alcohol open i-mer
B_{II}^F	free contribution to second virial coefficient of component I
C_{JI}, D_{JI}	coefficients of eqn. (16)
F	objective function as defined by eqn. (19)
H^E	excess molar enthalpy
h_A	enthalpy of hydrogen bond formation for acid dimer
h_{AB}	enthalpy of complex formation between components A and B
h_B	enthalpy of a hydrogen bond formation for alcohol
K_A	equilibrium constant of acid dimer formation
K_{AB}	solvation constant between components A and B
K_B	association constant of alcohol open-chain i-mer formation
N	number of experimental data points

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P	total pressure
P_I^s	saturated vapour pressure of pure component I
q_I	molecular geometric area parameter of pure component I
R	universal gas constant
r_I	molecular geometric volume parameter of pure component I
T	absolute temperature
V	true molar volume of acid + alcohol mixture given by eqn. (10)
V_A^0, V_B^0	true molar volumes of pure acid and alcohol given by eqns. (11) and (12), respectively
v_I^L	pure liquid molar volume of component I
x_I	liquid-phase mole fraction of component I
y_I	vapour-phase mole fraction of component I
y_{I_1}	vapour-phase mole fraction of monomeric component I
Z	lattice coordination number, here set as 10

Greek letters

γ_I	activity coefficient of component I
θ_I	surface fraction of component I
σ_P, σ_T, σ_x, σ_y	standard deviations in pressure, temperature, liquid and vapour compositions, respectively
τ_{JI}	coefficient as defined by $\exp(-a_{JI}/T)$
Φ_I	segment fraction of component I
Φ_{I_1}	monomer segment fraction of component I
$\Phi_{A_1}^0$, $\Phi_{B_1}^0$	monomer segment fractions of pure acid and alcohol given by eqns. (13) and (14), respectively
ϕ_I	fugacity coefficient of component I at P and T
ϕ_I^s	fugacity coefficient of pure component I at P_I^s and T

Subscripts

A, B	acid and alcohol
A_1, A_2	acid monomer and acid dimer
AB	binary complex
B_1, B_i	alcohol monomer and alcohol open i-mer
chem	chemical
I, J, K	components I, J, and K
phys	physical

Superscripts

0	pure liquid reference state
*	323.15 K

INTRODUCTION

The dimerization constants and enthalpies of hydrogen-bond formation of alkanoic acids have been estimated [1] and vapour–liquid equilibria and excess molar enthalpies of mixtures of alkanoic acids with hydrocarbons have been well reproduced by using the UNIQUAC associated-solution model [2]. The UNIQUAC associated-solution model has shown its good performance in the correlation and prediction of vapour–liquid and liquid–liquid equilibria and excess molar enthalpies for alcohol solutions [3–6].

In this paper, we apply the UNIQUAC associated-solution model for the correlation of vapour-liquid equilibria and excess molar enthalpies of mixtures involving an alkanoic acid and an alcohol and for the prediction of ternary excess molar enthalpies of ethanoic acid + methanol + tetrachloromethane from binary information alone.

SOLUTION MODEL

According to the UNIQUAC associated-solution model, we assume that the alkanoic acid (A) and the alcohol (B) exist in the solution as dimers (A_2) and open chains (B_i), and that acid monomers and alcohol open chains lead to chemical complexes AB_i. The equilibrium constants for these complex-forming reactions are defined by

$$K_A = \frac{\Phi_{A_2}}{\Phi_{A_1}^2}\frac{1}{2} \quad \text{for } A_1 + A_1 = A_2$$

$$= K_A^* \exp\left[-\frac{h_A}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{1}$$

$$K_B = \frac{\Phi_{B_{i+1}}}{\Phi_{B_i}\Phi_{B_1}}\frac{i}{i+1} \quad \text{for} \quad B_i + B_1 = B_{i+1}$$

$$= K_B^* \exp\left[-\frac{h_B}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{2}$$

$$K_{AB} = \frac{\Phi_{AB_i}}{\Phi_{A_1}\Phi_{B_i}}\frac{i}{r_A + ir_B} \quad \text{for } A_1 + B_i = AB_i$$

$$= K_{AB}^* \exp\left[-\frac{h_{AB}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \tag{3}$$

Activity coefficient

The activity coefficient of associating component I is given by

$$\ln \gamma_I = \ln\left(\frac{\Phi_{I_1}}{\Phi^0_{I_1} x_I}\right) + r_I\left(\frac{1}{V^0_I} - \frac{1}{V}\right) - \left(\frac{Z}{2}\right) q_I \left[\ln\left(\frac{\Phi_I}{\theta_I}\right) + 1 - \frac{\Phi_I}{\theta_I}\right] + q_I\left[1 - \ln\left(\sum_J \theta_J \tau_{JI}\right) - \sum_J \frac{\theta_J \tau_{I,J}}{\sum_K \theta_K \tau_{KJ}}\right] \tag{4}$$

where Z is the lattice coordination number taken as 10 and the segment fraction Φ_I, the surface fraction θ_I, the binary coefficient τ_{JI} related to the binary interaction parameter a_{JI} are expressed by

$$\Phi_I = r_I x_I \Big/ \sum_J r_J x_J \tag{5}$$

$$\theta_I = q_I x_I \Big/ \sum_J q_J x_J \tag{6}$$

$$\tau_{JI} = \exp(-a_{JI}/T) \tag{7}$$

The monomer segment fractions of both associating components are solved simultaneously from eqns. (8) and (9)

$$\Phi_A = \Phi_{A_1} + 2K_A\Phi^2_{A_1} + \frac{K_{AB}\Phi_{A_1}\Phi_{B_1}r_A}{1 - K_B\Phi_{B_1}} \tag{8}$$

$$\Phi_B = \frac{\Phi_{B_1}}{(1 - K_B\Phi_{B_1})^2}(1 + K_{AB}\Phi_{A_1}r_B) \tag{9}$$

The true molar volume of the mixture is given by

$$\frac{1}{V} = \frac{\Phi_{A_1}}{r_A}(1 + K_A\Phi_{A_1}) + \frac{\Phi_{B_1}}{r_B(1 - K_B\Phi_{B_1})} + \frac{K_{AB}\Phi_{A_1}\Phi_{B_1}}{1 - K_B\Phi_{B_1}} \tag{10}$$

At pure liquid states, eqn. (10) reduces to eqns. (11) and (12) and the monomer segment fractions $\Phi^0_{A_1}$ and $\Phi^0_{B_1}$ are expressed by eqns. (13) and (14)

$$\frac{1}{V^0_A} = \frac{1 - K_A\Phi^{02}_{A_1}}{r_A} \tag{11}$$

$$\frac{1}{V^0_B} = \frac{1 - K_B\Phi^0_{B_1}}{r_B} \tag{12}$$

$$\Phi^0_{A_1} = [-1 + (1 + 8K_A)^{0.5}]/4K_A \quad (13)$$

$$\Phi^0_{B_1} = [2K_B + 1 - (1 + 4K_B)^{0.5}]/2K_B^2 \quad (14)$$

Excess molar enthalpy

The excess molar enthalpy of the acid-alcohol mixture is expressed as the sum of the chemical and physical contributions

$$\begin{aligned} H^E &= H^E_{\text{chem}} + H^E_{\text{phys}} \\ &= h_A x_A K_A\left(\frac{\Phi^2_{A_1}}{\Phi_A} - \Phi^{02}_{A_1}\right) + h_B x_B K_B(\Phi_{B_1} - \Phi^0_{B_1}) \\ &\quad + h_{AB} K_{AB} r_B \Phi_{A_1} x_B \frac{(1 - K_B\Phi_{B_1})}{(1 + K_{AB} r_B \Phi_{A_1})} \\ &\quad - R \sum_I q_I x_I \frac{\sum_J \theta_J \frac{\partial \tau_{JI}}{\partial(1/T)}}{\sum_J \theta_J \tau_{JI}} \end{aligned} \quad (15)$$

The binary interaction parameters are assumed to be linearly dependent on temperature

$$a_{JI} = C_{JI} + D_{JI}(T - 273.15) \quad (16)$$

CALCULATED RESULTS

Vapour–liquid equilibrium data were reduced using the thermodynamic relation

$$P\phi_I y_I = \gamma_I x_I \phi^s_I P^s_I \left[\frac{v^L_I(P - P^s_I)}{RT}\right] \quad (17)$$

where P is the total pressure, y_I the vapour-phase mole fraction of component I, P^s_I the pure component vapour pressure taken from the original vapour–liquid equilibrium data set, and v^L_I the pure-liquid molar volume estimated from the modified Rackett equation [7]. The fugacity coefficient ϕ_I is calculated from the chemical theory of vapour imperfections [8]

$$\phi_I = \frac{y_{I_1}}{y_I} \exp\left(\frac{PB^F_{II}}{RT}\right) \quad (18)$$

where y_{I_1} is the vapour-phase monomer mole fraction of component I and

TABLE 1

Association parameters and molecular structural parameters for pure components

Component A	K_A at 323.15 K	$-h_A$/ kJ mol^{-1}	r_A	q_A
Methanoic acid	15899.8	46.6	1.24	1.19
Ethanoic acid	14651.2	44.5	1.78	1.62
Propanoic acid	11948.5	47.9	2.32	2.05
Butanoic acid	11274.5	45.1	2.86	2.49
Methanol	173.9	23.2	1.15	1.12
Ethanol	110.4	23.2	1.69	1.55
1-Propanol	87.0	23.2	2.78	2.51
2-Propanol	49.1	23.2	2.78	2.51
1-Butanol	69.5	23.2	2.77	2.42
Tetrachloromethane			2.71	2.37

B_{II}^{F} is the free contribution to the second virial coefficient [9]. Values of the critical constants and related parameters to evaluate v_{I}^{L}, B_{II}^{F} and the dimerization contribution to the second virial coefficient are available from Ambrose and Ghiassee [10] and Reid et al. [11].

The association parameters of the pure acids and alcohols were taken from Tamura and Nagata [1], Brandani [12] and Stokes and Burfitt [13], and the pure component molecular structural parameters, r and q, were calculated from the method of Vera et al. [14]. These values are given in Table 1. The solvation parameters are shown in Table 2.

TABLE 2

Solvation parameters for binary mixtures

System (A + B)	K_{AB} at 323.15 K	$-h_{AB}$/ kJ mol^{-1}
Methanoic acid + 1-propanol	450	32
Methanoic acid + 2-propanol	350	32
Methanoic acid + 1-butanol	400	32
Ethanoic acid + methanol	500	32
Ethanoic acid + ethanol	400	32
Ethanoic acid + 1-propanol	350	32
Ethanoic acid + 2-propanol	300	32
Ethanoic acid + 1-butanol	320	32
Propanoic acid + methanol	400	32
Propanoic acid + 2-propanol	280	32
Propanoic acid + 1-butanol	280	32
Butanoic acid + methanol	380	32
Methanol + tetrachloromethane	1.5	5.5

TABLE 3

The results of fitting the UNIQUAC associated-solution model to vapour–liquid equilibrium data and root-mean-square deviations δP, δT, δx and δy for binary acid + alcohol systems

System (A + B)	Temp. K	Number of data points	Energy parameters		Root-mean-square deviations				Ref.
			a_{AB}/K	a_{BA}/K	δP/Torr	δT/K	$\delta x \times 10^3$	$\delta y \times 10^3$	
Methanoic acid + 1-butanol[a]	298.15	9	865.26	−364.45	3.18	0.00	1.1	10.0	16
Methanoic acid + 1-butanol[a]	308.15	9	929.54	−380.39	2.73	0.00	1.4	12.9	
Methanoic acid + 1-butanol[a]	318.15	9	903.56	−377.72	2.55	0.00	1.5	13.0	
Ethanoic acid + methanol[a]	308.15	9	−347.68	−3.08	2.87	0.00	1.2	6.4	17
Ethanoic acid + methanol[a]	318.15	9	−363.64	20.83	1.83	0.00	1.1	7.0	
Ethanoic acid + ethanol[a]	308.15	13	−267.06	−7.86	2.00	0.00	1.4	7.9	17
Ethanoic acid + ethanol[a]	318.15	13	−262.74	−31.59	2.06	0.00	1.2	6.1	
Ethanoic acid + 1-butanol[a]	298.15	10	−92.06	−126.20	1.24	0.00	1.7	13.6	18
Ethanoic acid + 1-butanol[a]	308.15	10	−41.28	−164.23	1.84	0.00	1.4	12.4	
Ethanoic acid + 1-butanol[a]	318.15	10	−16.19	−174.96	2.85	0.00	1.3	11.6	
Propanoic acid + methanol[a]	298.18	16	−298.39	9.64	1.59	0.00	2.0	7.3	19
Propanoic acid + methanol[b]	300.07	32	−281.96	−9.17	1.04	0.00	0.5	4.0	
Propanoic acid + methanol[b]	308.21	31	−288.11	−9.00	1.46	0.00	0.9	6.5	
Propanoic acid + methanol[b]	318.16	32	−294.37	−6.36	1.91	0.00	1.3	7.2	
Butanoic acid + methanol[b]	301.75	16	−299.81	57.63	2.07	0.00	1.3	5.3	19
Butanoic acid + methanol[b]	308.26	16	−301.37	59.00	2.22	0.00	1.8	5.6	
Butanoic acid + methanol[b]	312.62	16	−295.39	48.35	2.32	0.00	3.1	5.7	
Butanoic acid + methanol[b]	318.20	16	−291.67	40.59	2.33	0.00	2.3	5.4	

[a] Vapour mole fractions were evaluated by a numerical procedure given by Miksch et al. [20]. [b] Vapour mole fractions were calculated by a method described by Fredenslund et al. [21].

An optimum set of the energy parameters was sought by minimizing the objective function [15]

$$F = \sum_{i=1}^{N} \left[\frac{(P_i - \hat{P}_i)^2}{\sigma_P^2} + \frac{(T_i - \hat{T}_i)^2}{\sigma_T^2} + \frac{(x_{1i} - \hat{x}_{1i})^2}{\sigma_x^2} + \frac{(y_{1i} - \hat{y}_{1i})^2}{\sigma_y^2} \right] \quad (19)$$

where a circumflex denotes the most probable calculated value corresponding to each measured variable. The standard deviations of the measured values are: for pressure, $\sigma_P = 1$ Torr; for temperature, $\sigma_T = 0.05$ K; for liquid-phase mole fraction, $\sigma_x = 0.001$; for vapour-phase mole fraction, $\sigma_y = 0.003$. Table 3 gives the results of vapour–liquid equilibrium data reduction and Figs. 1–4 show some typical examples.

Table 4 lists the binary results of the excess molar enthalpies. The coefficients, C_{JI} and D_{JI}, were obtained by minimizing the sum of the

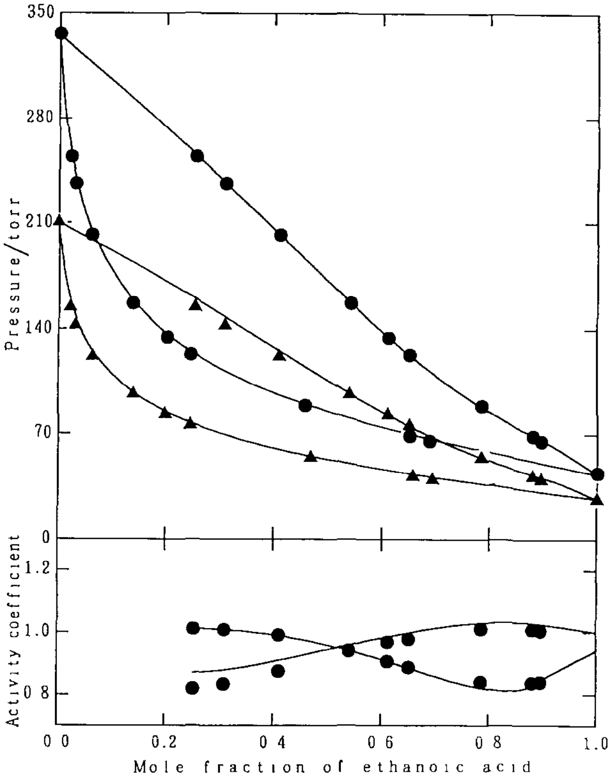

Fig. 1. Vapour–liquid equilibria for the ethanoic acid + methanol system. Calculated: ——; experimental [17]: ▲, 308.15 K; ●, 318.5 K.

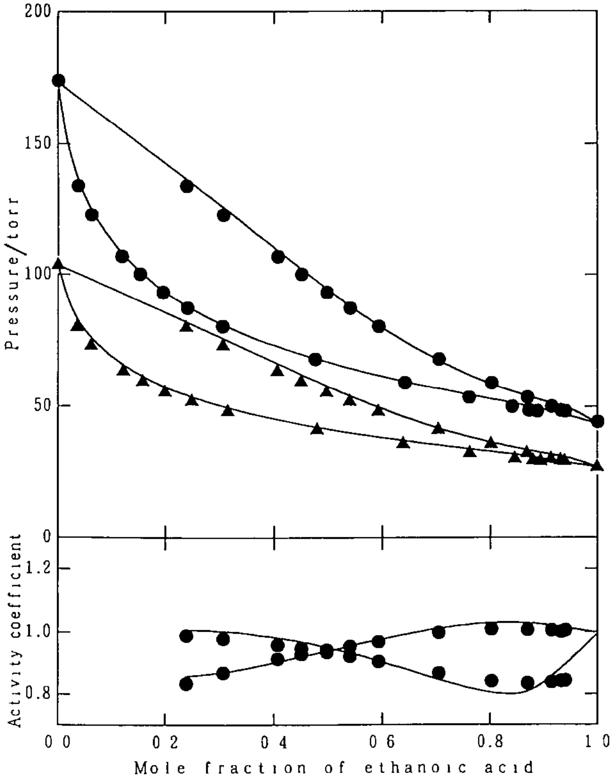

Fig. 2. Vapour–liquid equilibria for the ethanoic acid + ethanol system. Calculated: ——; experimental [17]: ▲, 308.15 K; ●, 318.15 K.

squares of the deviations between the experimental and calculated values. The simplex method of Nelder and Mead [25] was used for this purpose. Figures 5–8 compare the calculated values with the observed results for selected systems.

The ternary excess molar enthalpies of the ethanoic acid + methanol + tetrachloromethane system at 298.15 K were predicted using the UNIQUAC associated-solution model with the binary parameters given in Table 4. The absolute arithmetic mean deviation between the predicted and experimental values for 35 data points [26] is 26.03 J mol^{-1}.

We may conclude that the UNIQUAC associated-solution model is useful in the correlation of vapour–liquid equilibrium and excess molar enthalpy data of binary acid + alcohol mixtures and could be used for the prediction of ternary excess molar enthalpy data of solutions including an acid, an alcohol and one non-associated component.

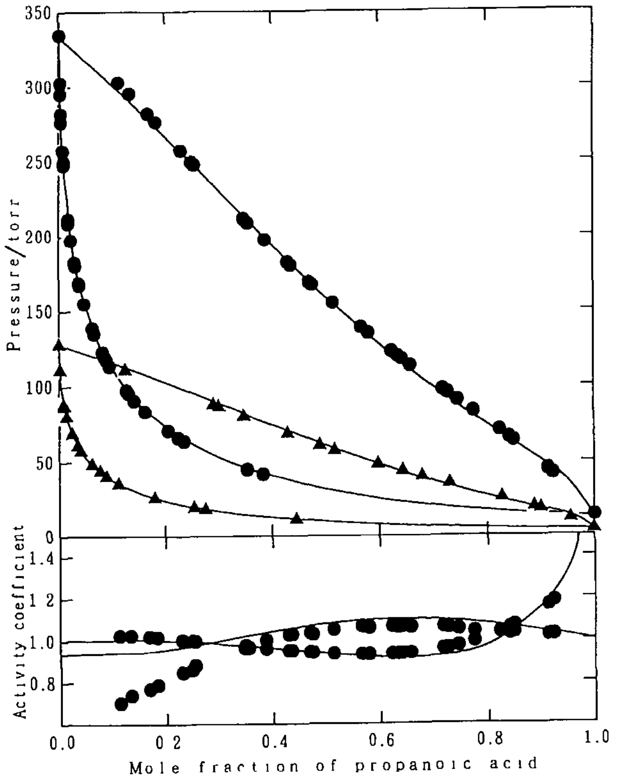

Fig. 3. Vapour–liquid equilibria for the propanoic acid + methanol system. Calculated: ——; experimental [19]; ▲, 298.18 K; ●, 318.16 K.

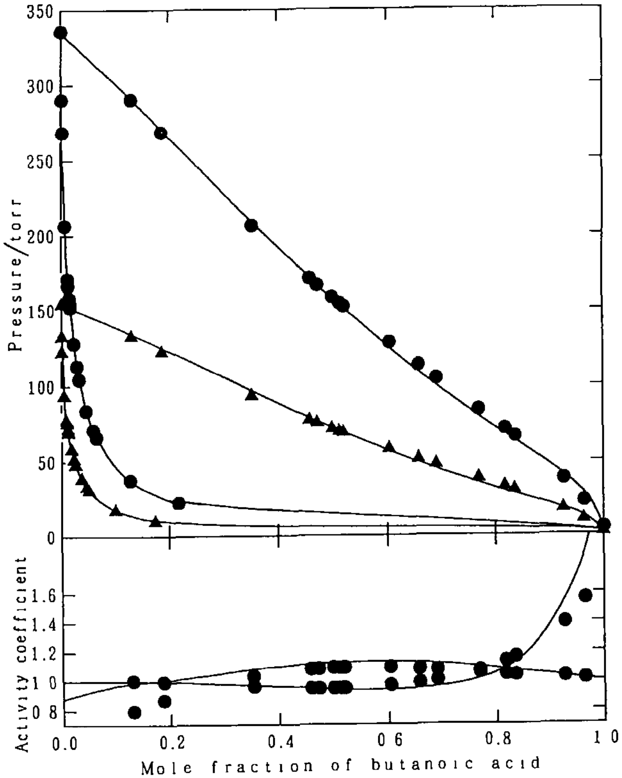

Fig. 4. Vapour–liquid equilibria for the butanoic acid + methanol system. Calculated: ——; experimental [19]: ▲, 301.75 K; ●, 318.20 K.

TABLE 4

The results of fitting the UNIQUAC associated-solution model to excess molar enthalpies of binary mixtures at 298.15 K

System (A + B)	Number of data points	Parameters				Deviations[a]		Ref.
		C_{AB}/K	C_{BA}/K	D_{AB}	D_{BA}	AAM/ J mol^{-1}	RMS/ J mol^{-1}	
Methanoic acid + 1-propanol	19[b]	700.45	225.20	4.1375	2.5392	5.41	6.00	22
Methanoic acid + 2-propanol	19	1123.69	121.10	28.8885	2.0340	9.65	10.91	22
Methanoic acid + 1-butanol	19	853.99	226.82	5.2450	2.4085	2.91	3.39	22
Ethanoic acid + methanol	19	991.98	31.68	6.9597	1.1175	0.87	1.36	22
Ethanoic acid + ethanol	19	940.97	197.78	6.2914	1.4682	0.82	1.20	22
Ethanoic acid + 1-propanol	19	962.92	431.02	5.9770	2.0505	5.17	5.88	22
Ethanoic acid + 2-propanol	19	801.37	122.51	4.7076	0.6691	8.65	10.20	22
Ethanoic acid + 1-propanol	19	1122.35	450.44	8.5736	2.0071	7.68	8.69	22
Propanoic acid + methanol	19	176.88	171.33	94.5072	1.7533	13.38	15.29	22
Propanoic acid + 2-propanol	19	1133.77	397.50	9.0842	2.0969	9.84	11.23	22
Propanoic acid + 1-butanol	19	1025.15	540.06	43.2225	2.8675	13.07	14.78	22
Butanoic acid + methanol	19	−138.10	−3954.65	0.0298	14.4560	14.77	16.45	22
Ethanoic acid + tetrachloromethane[c]	44	306.41	406.66	0.8252	1.3301	3.35	4.51	23
Methanol + tetrachloromethane	19	130.03	367.46	0.8833	2.1754	4.09	8.18	24

[a] AAM, absolute arithmetic mean deviation; RMS, root-mean-square deviation. [b] Experimental values are interpolated at 0.05 mole fraction intervals from the smoothing equation given by Hasse and Lorenz (1985) [22]. [c] $T = 293.15$ K.

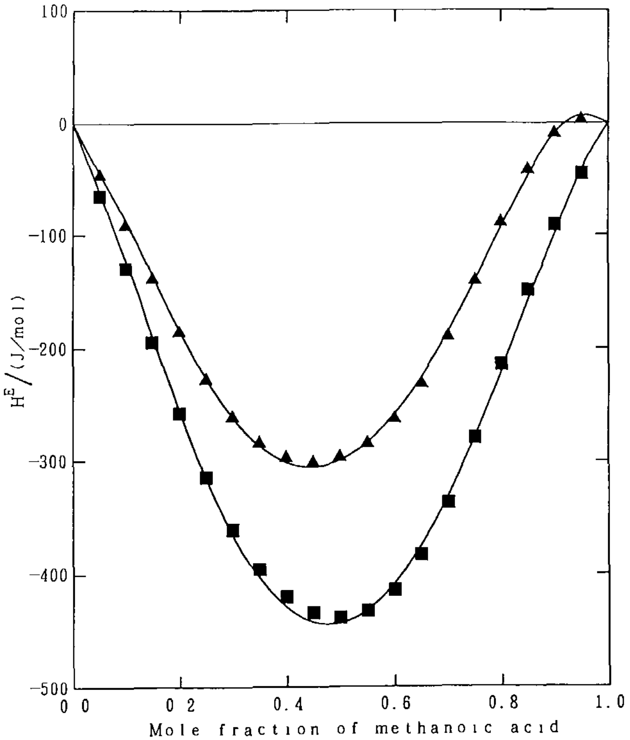

Fig. 5. Excess molar enthalpies for two methanoic acid + alcohol systems at 298.15 K. Calculated: ——; experimental [22]: ■, methanoic acid + 1-propanol; ▲, methanoic acid + 1-butanol.

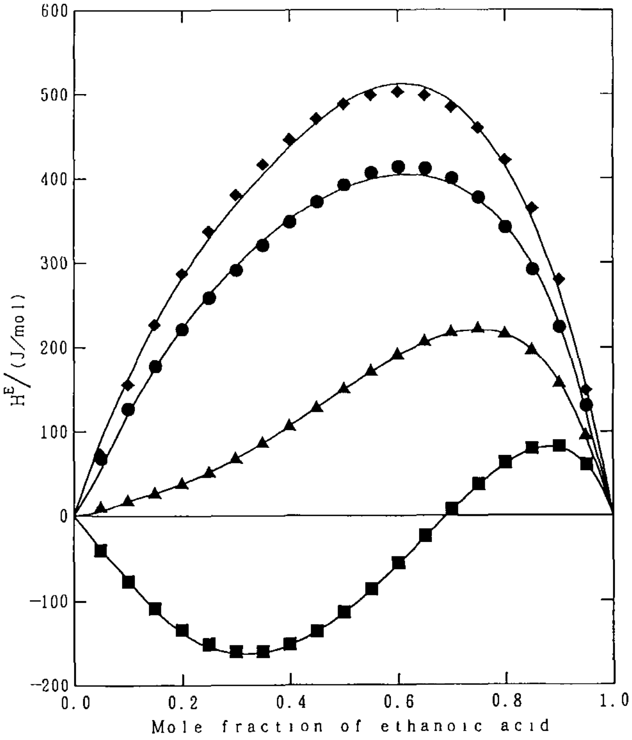

Fig. 6. Excess molar enthalpies for four ethanoic acid + alcohol systems at 298.15 K. Calculated: ——; experimental [22]: ■, ethanoic acid + methanol; ▲, ethanoic acid + ethanol; ●, ethanoic acid + 1-propanol; ◆, ethanoic acid + 1-butanol.

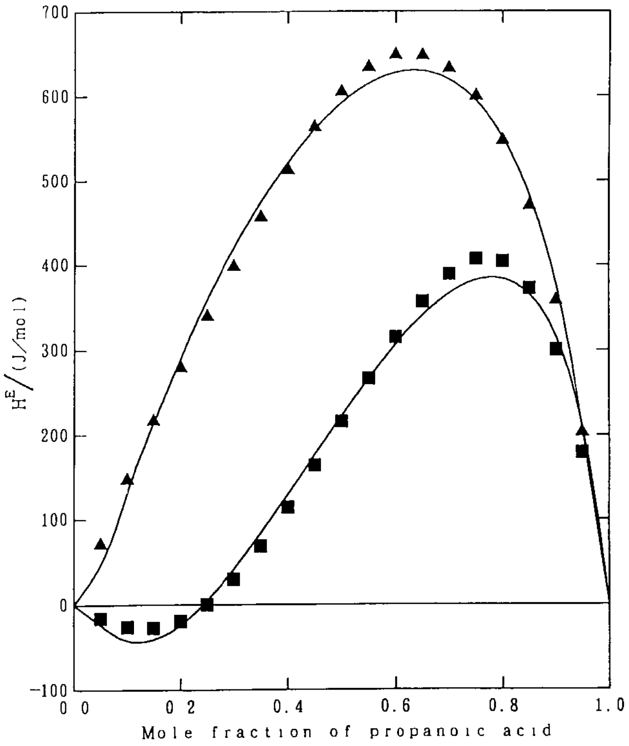

Fig. 7. Excess molar enthalpies for two propanoic acid + alcohol systems at 298.15 K. Calculated: ——; experimental [22]: ■, propanoic acid + methanol; ▲, propanoic acid + 1-butanol.

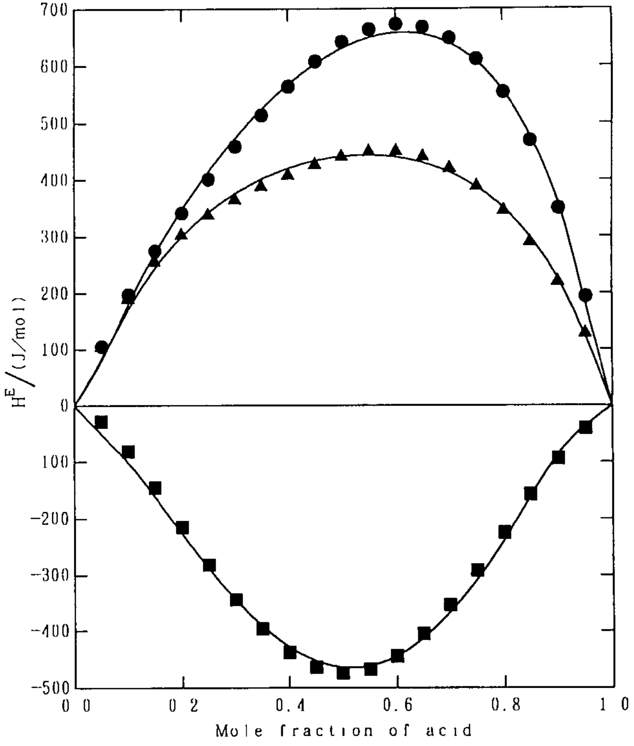

Fig. 8. Excess molar enthalpies for three acid + 2-propanol systems at 298.15 K. Calculated: ——; experimental [22]: ■, methanoic acid + 2-propanol; ▲, ethanoic acid + 2-propanol; ●, propanoic acid + 2-propanol.

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